10/510146

DT04 Rec'd PCT/PTO 03 OCT 2004

Method of making a heating element of molybdenum silicide type and a heating element.

The present invention relates to a method of manufacturing a heating element of the molybdenum silicide type and also to a heating element.

An electric resistance element of the molybdenum silicide type is described in Swedish Patent Specifications 0003512-1 and 0004329-9. According to patent specification 0003512-1 the resistance material of the heating element includes $Mo(Si_{1-x}Al_x)_2$ which is caused to contain aluminium to an extent at which the formation of pest is essentially prevented.

It has been found that when such material is operated in a temperature range of 400 - 600°C no pest, or only a slight amount of pest, is formed. Pest is formed by virtue of the formation of MoO_3 from $MoSi_2$ and O_2.

The reason why the formation of pest is significantly reduced or is eliminated is due the formation of Al_2O_3 on the surface of the element.

According to one preferred embodiment x is caused to lie in the range of 0.2 - 0.6.

The other patent specification 0004329-9 teaches a method of increasing the useful life span of heating elements that consist chiefly of molybdenum silicide and alloys of this basic material where the element operates at high temperatures.

According to this patent specification, the heating element is caused to contain aluminium to an extent which is suffi-

cient to maintain a stable, slowly growing layer of aluminium oxide on the surface of the heating element.

According to a preferred embodiment the heating element material is caused to contain $Mo(Si_{1-x}Al_x)_2$ where x lies in the range of 0.2 - 0.6.

A material of the molybdenum silicide type that contains aluminium has been found to possess improved corrosion properties at both low and high temperatures.

Such material is often produced by mixing $MoSi_2$ powder with oxidic raw material, such as aluminosilicates. When the raw material is bentonite clay, there is obtained a relatively low melting point which contributes towards so-called smelt phase sintering which results in dense materials that contain $MoSi_2$ and a proportion of aluminium silicate corresponding to 15 - 20 percent by volume.

Bentonite clay has different compositions. Some bentonites include 60% by weight SiO_2 while some contain somewhat more than 70% by weight SiO_2. Although the Al_2O_3 content varies, it normally lies between 13 - 20% by weight. The melting point varies between about 1200 - 1400°C.

Bentonite clay that contains chiefly SiO_2 can be used in the production of heating elements containing $Mo(Si_{1-x}Al_x)_2$. When sintering with an Al-alloyed silicide there takes place a chemical exchange reaction in which the greater affinity of the oxygen to Al than to Si results in Si leaving the aluminium silicate and entering the silicide as a result of Al leaving the silicide and being sucked up by the oxide phase. This exchange reaction also contributes towards improved sin-

tering properties of the composite material. The final material contains $Mo(Si_{1-x}Al_x)_2$ that is substantially deplete of Al, where the oxide phase contains Al_2O_3 in all essentials.

The standard procedure of manufacture involves mixing molybdenum, silicon and aluminium in powder form and firing the powder mix normally under a shielding gas atmosphere. This results in a cake of the material $Mo(Si_{1-y}Al_y)_2$, where y is larger than x as a result of said exchange reaction. The reaction is exothermic. The cake is then crushed and ground down to a fine particle size normally in the order of 1 - 20μm. This powder is mixed with bentonite clay such as to form a wet ceramic material. The material is extruded and dried to a rod form whose diameter corresponds to the diameter of the subsequent heating element. The material is then sintered at a temperature that exceeds the melting temperature of the including components.

However, there is a drawback with an element of this kind. The problem is that the oxide that forms on the surface of the element, namely Al_2O_3, sometimes peels away or flakes off, i.e. loosens from the surface of the element in cyclic operation.

A peeling oxide gives poorer protection against continued oxidation of aluminium which becomes impoverished in the outer surface of the element more quickly. Moreover, peeling oxide can contaminate the oven in which the element is fitted, with the risk that performance and the appearance of products heat treated in ovens that have such elements will be significantly impaired. This restricts the use of such elements in heating processes.

This problem is solved by the present invention.

The present invention thus relates to a method of producing a heating element that is comprised substantially of the molybdenum silicide type and alloys of this basic material and is characterised by producing a material that contains chiefly $Mo(Si_{1-x}Al_x)_2$ and Al_2O_3 by mixing molybdenum aluminosilicide ($Mo(Si_{1-y}Al_y)_2$) with bentonite clay in a way known per se, where the bentonite clay is caused to include impurities with which the molybdenum silicide cannot be alloyed and with which the symmetry of the crystal lattice of the molybdenum silicide will be retained, with a combined content of 2000 ppm.

The present invention also relates to a heating element of the kind having the significant features set forth in the accompanying Claim 7.

The invention will be described in more detail in the following.

In accordance with the invention, a heating element that consists chiefly of molybdenum silicide type and alloys of this basic material is produced in principle by the method described above. There is thus produced a powder that contains essentially $Mo(Si_{1-y}Al_y)_2$ which is mixed with bentonite clay that contains Al_2O_3.

According to the invention, the bentonite clay is caused to include impurities with which the molybdenum silicide cannot be alloyed, so that the symmetry of the crystal lattice will be retained, with a combined content of less than 2000 ppm. Bentonite clay that has these low impurity contents can be

produced by purifying the bentonite clay with the aid of known chemical cleaning processes.

In distinction to this approach, it is possible to partly substitute molybdenum with Re or W in the material $Mo(Si_{1-x}Al_x)_2$ without changing the symmetry of the crystal lattice.

According to one preferred embodiment of the invention, the combined content of the impurity substances Mg, Ca, Fe, Na and K is caused to be below 2000 ppm.

According to another preferred embodiment of the invention, the content of said impure substances is caused to be below 1000 ppm.

It has been found surprisingly that there is obtained at such low contaminant contents an oxide which does not peel after cyclic operation between room temperature and high temperature, for instance 1500°C.

According to one embodiment x is caused to lie in the range of 0.4 - 0.6.

According to one preferred embodiment x is caused to lie in the range of 0.45 - 0.55.

The present invention thus solves the problem mentioned in the introduction and enables the present element to be used beneficially in ovens without detriment to the material treated in the oven.

The present invention shall not be considered to be limited

to the aforedescribed embodiments since variations can be made within the scope of the accompanying claims.